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# Study on the suppression effect of natural zeolite on expansion of concrete due to alkali–aggregate reaction

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*The effect and mechanism of natural zeolite on preventing expansion due to alkali–aggregate reaction are studied in this paper. The results confirm that the expansion can be minimized by increasing the fineness of natural zeolite powder (even to superfineness) or by a previous heat-treatment for the zeolite additive.*

## Introduction

Recently, a systematic investigation has shown that reactive aggregates are widely distributed throughout China.[1] Destruction of concrete structures caused by alkali-aggregate reaction (AAR) has been found in some regions in China, such as Beijing, Shanghai, Sandong province, etc. Up to now, there has been no fundamental remedial method for the destruction caused by AAR to buildings. In general, it is known that adding mineral additives to concrete is an effective measure for preventing AAR. Investigations have been carried out on the effects of silica fume, fly ash and blast furnace slag used as mineral additives for suppressing AAR in some countries.

In our investigation, natural zeolite was chosen as a new mineral additive for concrete. The suppression effects of its content and fineness on AAR were systematically studied. Comparison tests with fly ash, blast furnace slag and silica fume were also performed. Finally, a desirable effect on preventing expansion caused by AAR was found in which a typical reactive aggregate from the Beijing Yong Dinghe River region was used.

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## Materials used and properties

### *Reactive aggregates*

Two kinds of synthetic reactive aggregates were used in the tests: hard glass (aggregate A) and dacite (aggregate B).

One natural reactive aggregate was also used (aggregate C), which was from the Beijing Yong Dinghe River region. Its mineral compounds are mainly rhyolite and chert.

The reactivity and assessment of the above aggregates according to the ASTM Test Method for Potential Reactivity of Aggregates (Chemical Method) (C289) are given in Table 1 and Fig. 1 ($S_c$, content of $SiO_2$ solubilized in the solution; $R_c$, reduction of alkali in the solution).

Figure 1 shows that aggregates A and B are harmful to concrete and aggregate C possesses potential reactivity. $S_c$ represents the alkali-silicate gel content in concrete: the higher $S_c$ is, the greater the gel content. $R_c$ represents the degree of polymerization of the gel in concrete. When $S_c$ is given, an aggregate with large $R_c$ possesses a low degree of polymerization of silicon. An aggregate with a high $S_c/R_c$ ratio is harmful because of the high polymerization de-

*Table 1. Reactivity of reactive aggregates used*

| Aggregates | $R_c$: mmol/l | $S_c$: mmol/l | Assessment |
|---|---|---|---|
| A | 57·4 | 65·7 | be harmful |
| B | 87·49 | 984·1 | be harmful |
| C | 98·4 | 115·8 | be potentially harmful |



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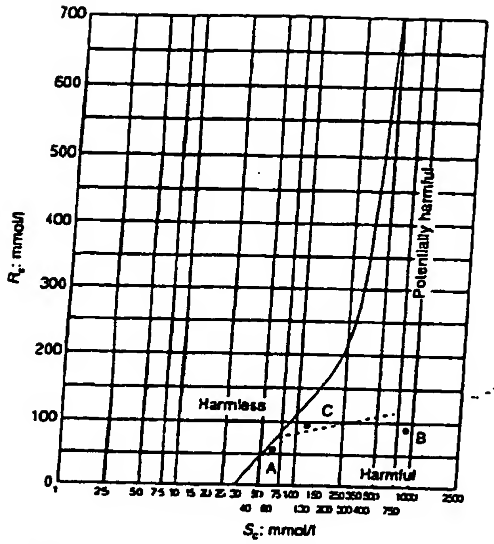


*Fig. 1. Reactivity of aggregates according to ASTM C289 (Chemical Method)*

gree of silicon. Aggregate A with $S_c/R_c = 1.14$ and aggregate B with $S_c/R_c = 11.26$ indicates that aggregate A possesses much lower reactivity than aggregate B.

### *Cement*

The cement used in the tests consisted of 96% clinker, originating from the Beijing Liu Lihe Cement Plant, and 4% natural gypsum. Its specific surface area was 5000 $cm^2/g$. Mineral composition of the clinker was as follows: $C_3S$, 33·92%; $C_2S$, 37·91%; $C_3A$, 4·80%; $C_4AF$, 15·96%.

To regulate the alkali content in cement, chemically pure NaOH was used.

### *Natural zeolite*

Two kinds of natural zeolite rock were used in the tests. One was Du Shikou natural zeolite rock from Chicheng county, Hebei province, China, and the other was Ohya-Rock natural zeolite rock from Japan. Their chemical compositions are shown in Table 2.

It was shown by X ray diffraction that these two zeolite rocks contain clinoptilolite.[2,3] The former contains 65% zeolite, while the latter contains 60% zeolite. Their fineness is shown in Table 3. Fineness levels I, II, III and IV correspond to 2510, 5280, 6860 and 8820, respectively.

### *Fly ash and slag*

The chemical composition and physical properties of the fly ash and blast furnace slag used in the tests are shown in Tables 4 and 5.

*Table 5. Physical properties of the fly ash and slag used*

| Materials | Density: $g/cm^3$ | Specific surface area: $cm^2/g$ | Residue on 0·08 mm sieve: % |
|---|---|---|---|
| Fly ash | 2·27 | 7040 | 0·4 |
| Slag | 2·96 | 6340 | 1·4 |

*Table 2. Chemical composition of natural zeolite rocks*

| Zeolite rock | Chemical composition: % | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ | $TiO_2$ | $P_2O_5$ | $Mn_2O$ | FeO | $H_2O^+$ | $H_2O$ | LOI |
| Du Shikou (China) | 67·71 | 11·22 | 1·12 | 1·10 | 2·64 | 1·55 | 2·65 | 0·11 | 0·08 | 0·04 | 0·17 | 7·52 | 4·74 | 10·00 |
| Ohya-Rock (Japan) | 70·17 | 11·81 | 1·61 | 0·52 | 2·54 | 2·73 | 1·91 | — | — | — | — | — | — | 8·71 |

*Table 3. Fineness of natural zeolite rocks*

| Zeolite rocks | Residue on 0·08 mm sieve: % | | | | Specific surface area by BET: $cm^2/g$ | | | |
|---|---|---|---|---|---|---|---|---|
| Du Shikou | 15·6 | 7·8 | 2·5 | 1·0 | 2510 | 5280 | 6960 | 8920 |
| Ohya-Rock | 8·0 | | | | 4800 | | | |

*Table 4. Chemical composition of the fly ash and slag used*

| Materials | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ | $TiO_2$ | LOI |
|---|---|---|---|---|---|---|---|---|---|
| Fly ash | 47·78 | 37·71 | 3·53 | 0·77 | 3·32 | 0·25 | 0·62 | 1·62 | 2·88 |
| Slag | 33·27 | 12·10 | 1·63 | 11·81 | 38·39 | 0·50 | 0·75 | 2·11 | 0·01 |

## Testing methods

All tests were performed in accordance with ASTM C221, C227 and C289 and GB 366-80.[4]

### *Proportion of mortar*

The cement to sand ratio was 1:2·25, and three mortar specimens 2·54 × 2·54 × 28·5 cm in size comprise a group. The water content enabling the flow of mortar to reach 105–120 mm was adopted.[5]

### *Compacting and curing*

Mortar specimens were compacted under constant conditions of 20 ± 2°C in a room, and cured in a special curing container in which the temperature was 38 ± 2°C and the relative humidity was higher than 95%.

### *Deformation measurement*

The length of mortar bars of different ages was measured by a type JDY-1 universal length-measuring instrument. Its measuring precision is about 0·001 mm.

### *Evaluation method*

According to SD105-82, when the linear free expansion of the mortar bar at 90 and 180 days is less than 0·05% and 0·1%, respectively, if the cement were used together with reactive aggregate, no harmful AAR would occur in concrete.

## Tests and results

### *Test series 1*

The effects of the fineness of natural zeolite powder on expansion caused by AAR with various dosages were investigated.

When reactive aggregate A was used, its content in aggregates was up to 100%, and the alkali content in cement was 1·4%. When reactive aggregate B was used, its content in aggregates was up to 20% (the remainder is quartz sand, which was used as a non-reactive aggregate), and the alkali content in cement was 2·2%.

The test results are shown in Figs 2–10.

From Figs 2–10, we can see the following:

(*a*) For aggregate A, the effect of natural zeolite with fineness I on preventing expansion due to AAR was not obvious, and there was little difference in the suppression effects between natural zeolites with finenesses II and III. The expansion of specimens with 20% natural zeolite was below 0·04% at 180 days. For zeolite with fineness I, when its content is more than 30% the suppressing effect on AAR was efficient.

(*b*) For aggregate B (with high reactivity), the fineness of the zeolite powder had a very marked effect on the expansion of the mortar bar. When the expansion of specimens at 91 days was less than 0·05%, to obtain the same effect it needed only 20% zeolite powder with fineness IV, but for the zeolite powder with finenesses II and III, it needed 30%, and for the zeolite powder with fineness I it needed 40%.

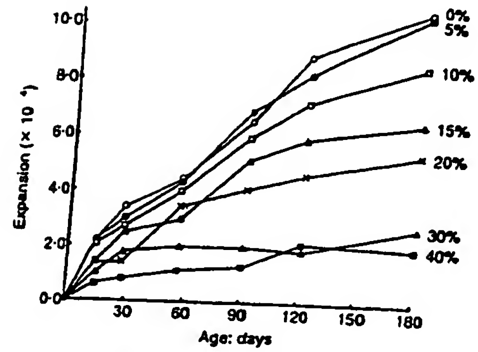


*Fig. 2. Effect of zeolite powder with fineness I on expansion caused by aggregate A*

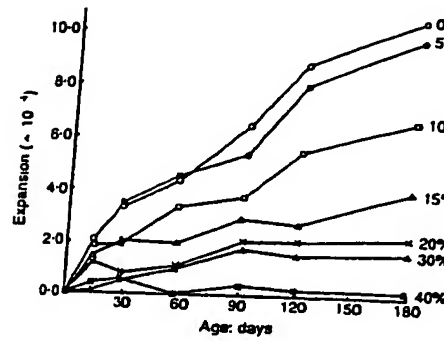


*Fig. 3. Effect of zeolite powder with fineness II on expansion caused by aggregate A*

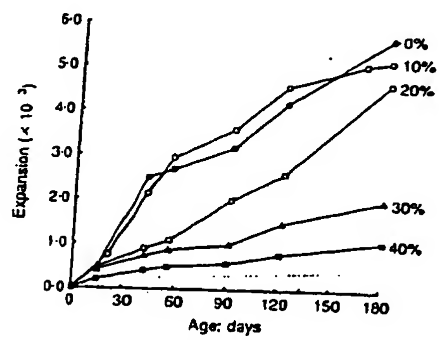


*Fig. 4. Effect of zeolite powder with fineness I on expansion caused by aggregate B*

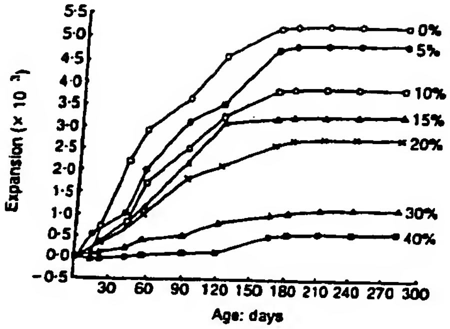


*Fig. 5. Effect of zeolite powder with fineness II on expansion caused by aggregate B*

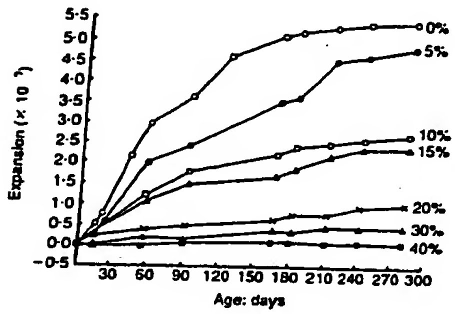


*Fig. 6. Effect of zeolite powder with fineness III on expansion caused by aggregate B*

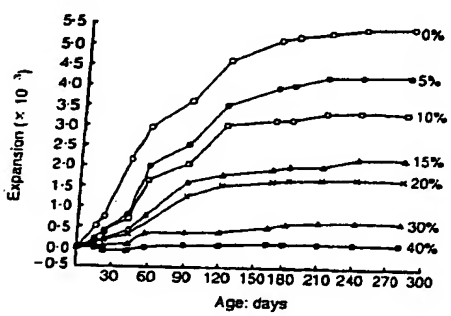


*Fig. 7. Effect of zeolite powder with fineness IV on expansion caused by aggregate B*

The inhibiting effect of natural zeolite powder on expansion due to AAR depends not only on its content in concrete, but also on its fineness.

### *Test series II*

The inhibiting effect of reactive zeolite on AAR was investigated.

Natural zeolite heated at 500°C for dehydration, and ground to a specific surface area of 4350 $cm^2/g$ (residue on a 0·008 mm sieve was 6·8%) was used. The sand consisted of 20% aggregate B and 80%

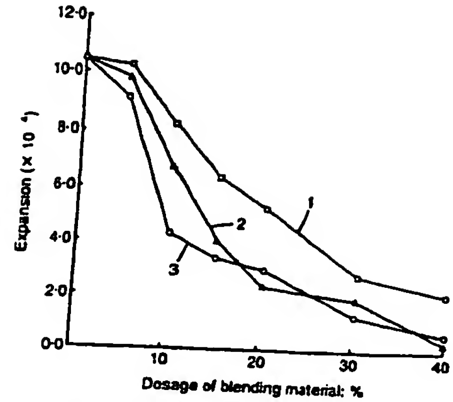


*Fig. 8. Effect of changes in zeolite powder fineness on expansion caused by aggregate A (at 180 days). 1. fineness level I; 2. fineness level II; 3. fineness level III*

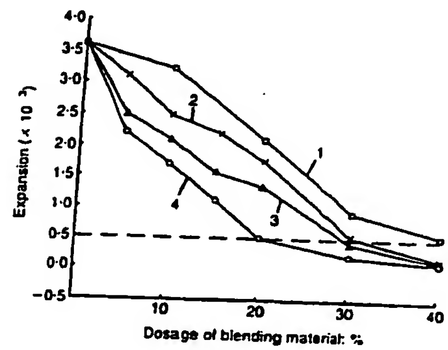


*Fig. 9. Effect of changes in zeolite powder fineness on expansion caused by aggregate B (at 90 days). 1. fineness level I; 2. fineness level II; 3. fineness level III; 4. fineness level IV*

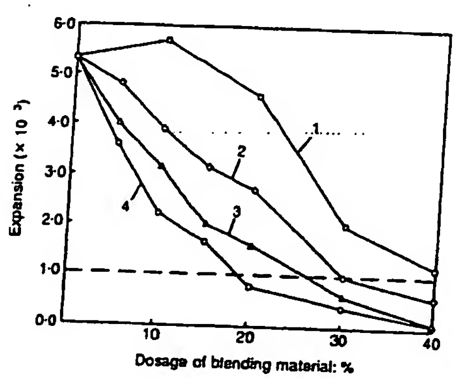


*Fig. 10. Effect of changes in zeolite powder fineness on expansion caused by aggregate B (at 180 days). 1. fineness level I; 2. fineness level II; 3. fineness level III; 4. fineness level IV*

quartz sand. The alkali content in the cement was regulated to 2·2%. The dosages of natural zeolite were 10, 20, 30 and 40% (by weight of total cement). The test results are shown in Fig. 11. The inhibition effects of heat-treated zeolite and normal zeolite on AAR are illustrated in Fig. 12.

From Fig. 12, it can be shown that when the content of heat-treated zeolite is more than 20%, the expansion of mortar bars at 56 days was below 0·05%. In comparison with normal zeolite (with the same content), the expansion of the mortar bar with added heat-treated zeolite can be reduced by 10–20%.

*Test series III*

The suppression effect of superfine zeolite powder (with a specific surface area of more than 10 000 $cm^2/g$) on AAR was investigated.

The sand used consisted of 20% aggregate B and 80% quartz sand. The alkali content in the cement was regulated to 2·2%. The zeolite contents were 10, 20, 30 and 40% (by mass of cement). The test results are shown in Figs 13 and 14.

From these figures, it can be shown that when the content of superfine zeolite powder was more than 10%, the expansion of the mortar bars was about 0·05% and 0·1% at 90 and 180 days, respectively. As a result, when the content of natural superfine zeolite

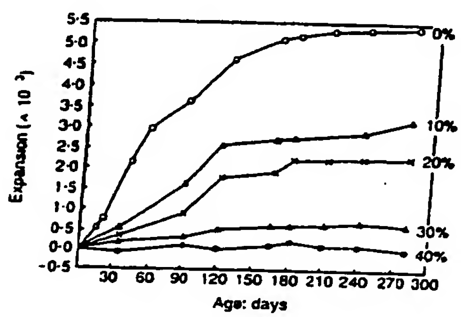


*Fig. 11. Inhibiting effect of heat-treated zeolite powder on AAR*

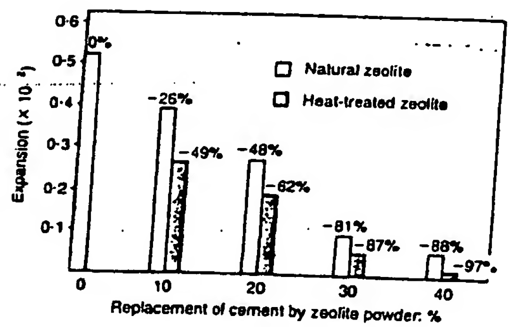


*Fig. 12. Comparison of the inhibiting effect on AAR between heat-treated zeolite and normal zeolite (at 180 days)*

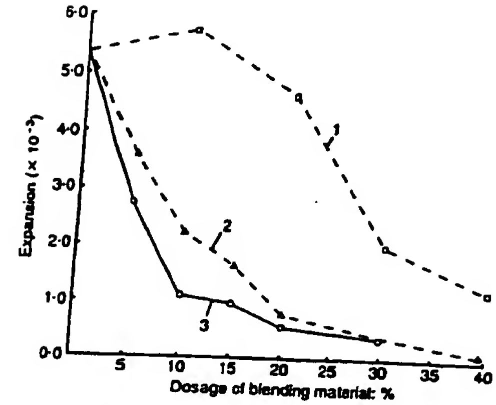


*Fig. 13. Inhibiting effect of superfine zeolite powder on AAR (at 90 days). 1, fineness level I; 2, fineness level IV; 3, superfine zeolite powder*

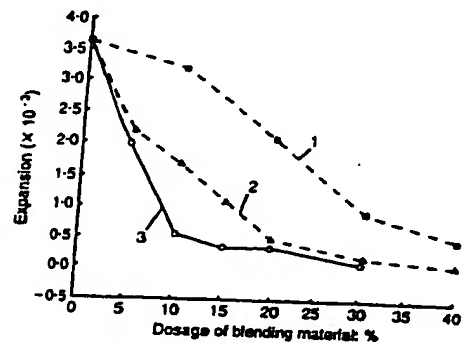


*Fig. 14. Inhibiting effect of superfine zeolite powder on AAR (at 180 days). 1, fineness level I; 2, fineness level IV; 3, superfine zeolite powder*

was more than 10%, the expansion of the mortar bar caused by AAR was suppressed efficiently.

*Test series IV*

The influence of the alkali content in cement was investigated.

Zeolite powder with a specific surface area of 7000 $cm^2/g$ was used. The sand consisted of 20% aggregate B and 80% quartz sand. The alkali content in cement was regulated by NaOH, and a plan of the test is shown in Table 6. The test results are illustrated in Fig. 15.

Figure 15 shows that for different dosages of zeolite powder the expansion of mortar caused by AAR increased with increasing alkali content in the cement. But with increasing dosages of zeolite the influence of the alkali content in the cement on the expansion of mortar decreased. When the dosage of zeolite was up to 30% the expansion of mortar was less than 0·05%, even though the alkali content in the cement was as high as 2·2%.

*Table 6. Influence of the alkali content in cement on inhibition*

| Sample | Alkali content in cement: % | Dosage of zeolite powder: % | Content of aggregate B in aggregate: % |
|---|---|---|---|
| 1 | 1·09 | 0, 10, 15, 20, 30 | 20 |
| 2 | 1·40 | 0, 10, 15, 20, 30 | 20 |
| 3 | 1·80 | 0, 10, 15, 20, 30 | 20 |
| 4 | 2·20 | 0, 10, 15, 20, 30 | 20 |

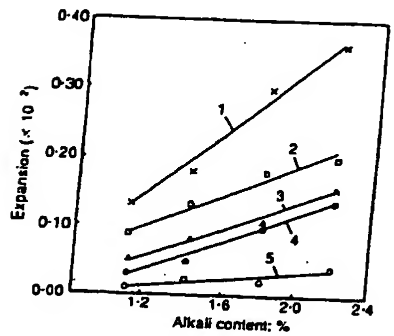


*Fig. 15. Influence of the alkali content in cement on the inhibiting effect on AAR. 1, control; 2, 10%; 3, 15%; 4, 20%; 5, 30%*

*Test series V*

This was a comparison test between Ohya-Rock natural zeolite rock from Japan and Du Shikuo natural zeolite rock from China. The properties of the zeolite rocks are as follows. Ohya-Rock natural zeolite rock is of the clinoplilolite type, with a zeolite content of 60% and a specific surface area of 4830 $cm^2/g$. Du Shikuo natural zeolite rock is also of the clinoplilolite type, with a zeolite content of 65% and specific surface area of 5280 $cm^2/g$.

The alkali content in the cement was 2·2%, and the sand used in the mortar consisted of 20% reactive aggregate B and 80% quartz sand.

The expansion of the mortar bar is shown in Fig. 16.

From Fig. 16, it can be seen that both kinds of zeolite rock have the same inhibiting effect on AAR associated with aggregate B. With a 30% dosage of zeolite, AAR in mortar can be inhibited.

*Test series VI*

The influence of different blending materials on AAR was investigated. Fly ash with a 7000 $cm^2/g$ specific surface area, blast furnace slag with 7000 $cm^2/g$, and silica fume with 200 000 $cm^2/g$ were used in the test. The plan of the test is shown in Tables 7 and 8. The test results are illustrated in Figs 17 and 18.

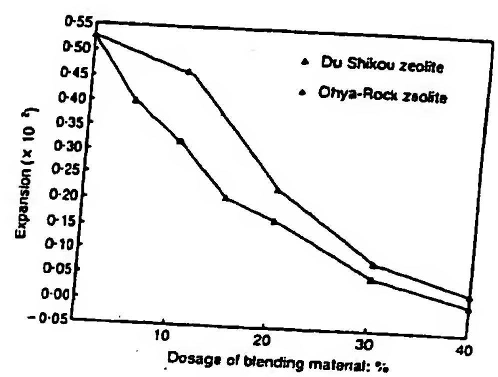


*Fig. 16. Comparison of the inhibiting effect on AAR between two kinds of natural zeolite*

*Table 7. Effects of various blending materials on AAR caused by reactive aggregate A*

| Sample | Blending materials | Dosage of blending materials: % | Reactive aggregate A: % | Total alkali content in cement: % |
|---|---|---|---|---|
| 1 | Natural zeolite | 0, 5, 10, 15, 20, 30, 40, | 100 | 1·4 |
| 2 | Fly ash | 0, 10, 15, 20, 30, 40, | 100 | 1·4 |
| 3 | Slag | 0, 10, 15, 20, 30, 40, | 100 | 1·4 |
| 4 | Silica fume | 0, 5, 10, 15, 20, | 100 | 1·4 |

*Table 8. Effects of various blending materials on AAR caused by reactive aggregate B*

| Sample | Blending materials | Dosage of blending materials: % | Reactive aggregate B: % | Total alkali content in cement: % |
|---|---|---|---|---|
| 5 | Natural zeolite | 0, 5, 10, 15, 20, 30, 40, | 20 | 2·2 |
| 6 | Fly ash | 0, 10, 15, 20, 30, 40, | 20 | 2·2 |
| 7 | Slag | 0, 10, 15, 20, 30, 40, 60 | 20 | 2·2 |
| 8 | Silica fume | 0, 5, 10, 15, 20, | 20 | 2·2 |

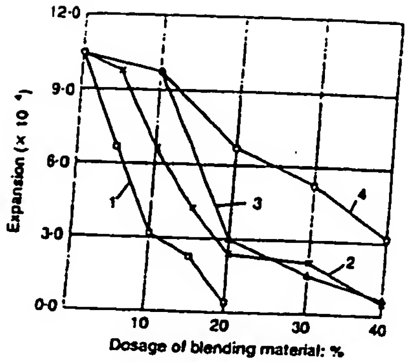


*Fig. 17. Influence of various blending materials on AAR caused by aggregate A (at 180 days). 1, sample 1; 2, sample 2; 3, sample 3; 4, sample 4*

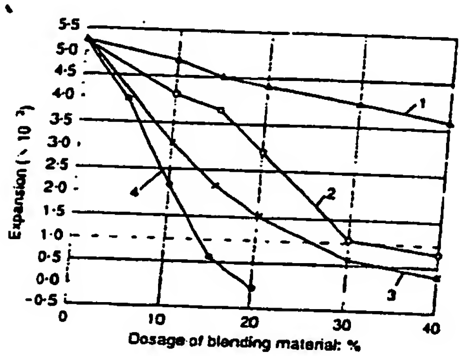


*Fig. 18. Influence of various blending materials on AAR caused by aggregate B (at 180 days). 1, sample 5; 2, sample 6; 3, sample 7; 4, sample 8*

From Fig. 17, it can be seen that for aggregate A, fly ash possesses the same inhibition effect on AAR as the zeolites. When the dosage was 20% the expansion of mortar was less than 0·03% at 180 days. However, to obtain the same effect, 10% silica fume and 40% slag were needed for silica fume to produce the best inhibiting effect on AAR.

From Fig. 18, we can see that for aggregate B, zeolite with a 30% dosage possesses the same inhibiting effect on AAR as 15% silica fume. The expansion of the mortar bar was about 0·05% at 180 days. However, when the dosage of fly ash was up to 30%, the expansion of the mortar bar at 180 days was double that with the silica fume. Slag possesses the least inhibiting effect on AAR among these three kinds of blending materials: the expansion of the mortar bar with a 40% content was 0·371% at 180 days.

*Test series VII*

Investigations carried out in recent years indicate that the AAR found in the Beijing region belongs to the alkali–silicate reaction type.[6] Some serious cases of destruction of concrete structures caused by AAR have been found in the Beijing region, for instance a three-dimensional cross bridge pier and an airport runway in Fu Chenmeng.

For a long period, the cement used in the Beijing region has had a high alkali content, while a large number of high-rise building constructions in this region have required the use of concretes. However, major use of high-strength cement or high early strength cement (without or with adding a little blending material) leads to the tendency of AAR in concrete. Thus, to ensure the durability of concrete structures in this region, and to reduce maintenance costs, investigations on AAR in this region and prevention techniques are needed urgently.

The Yong Dinghe River region is one of the main sources of sand and stone in Beijing. Initial investigations on aggregates from this region found that they contain a great deal of reactive mineral compounds, such as rhyolites, chert and dacite.[7] Typical rhyolites and chalcedonies were collected and prepared for the test in accordance with SD105-82.

Based on the above investigations, Du Shikuo zeolite powder with a specific surface area of 6960 $cm^2/g$ was used in the test, in which typical reactive aggregate from the Yong Dinghe River region was used. The test results are illustrated in Fig. 19.

It can be seen from Fig. 19 that the expansion of the mortar bar without adding zeolite at 90 and 180 days is more than 0·05 and 0·1%, respectively, which are the ASTM limiting values. Thus, aggregates from the Yong Dinghe River region are reactive aggregates, which can cause harmful expansion. When the dosage of zeolite was 5%, marked expansion still occurred, and the expansion of the mortar bar at 90 and 180 days was still more than the ASTM limits. However,

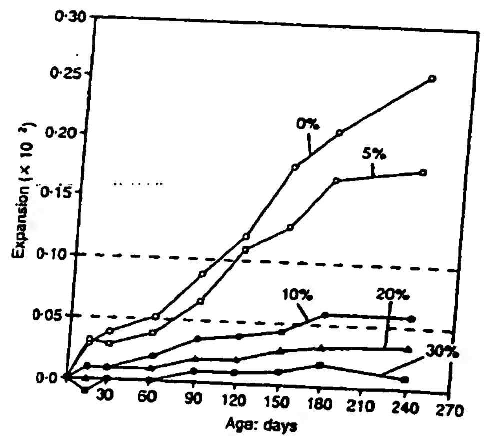


*Fig. 19. Inhibiting effect of natural zeolite powder on AAR caused by the reactive aggregate from the Yong Dinghe River region in Beijing*

when the dosage of zeolite was more than 10%, the expansion of the mortar was greatly reduced, to below the ASTM limits. When the zeolite dosage was 20 and 30%, AAR could be prevented efficiently.

## Conclusion

When there is an alkali content in cement, whether or not AAR will occur depends on the alkali reactivity of the aggregate, and the type of blending material and its fineness and dosage. The following conclusions can be drawn from this study:

(*a*) When 30% natural zeolite powder is used to replace the same content of cement (alkali content is 1·82%), AAR will not take place in concrete even if reactive aggregates are used.

(*b*) The inhibiting effect of natural zeolite powder on AAR is also related to its fineness.

For an aggregate with high alkali reactivity (e.g. aggregate B), to suppress AAR efficiently, 30% natural zeolite powder with a specific surface area of 5000–7000 $cm^2/g$ is needed. When the specific surface area is up to 9000 $cm^2/g$, about 20% natural zeolite powder is needed. When natural zeolite powder with a specific surface area of 10 000 $cm^2/g$ is used, only a content of 15% is needed to obtain the same inhibiting effect on AAR. However, if natural zeolite powder with a specific surface area of 2510 $cm^2/g$ is used, a content of 40% is required.

For an aggregate with normal alkali reactivity (e.g. aggregate A), when 20% natural zeolite powder with a specific surface area of 5000–7000 $cm^2/g$ is used AAR in concrete can be efficiently prevented, but for zeolite powder with a specific surface area of 2510 $cm^2/g$, 30% is needed to obtain the same inhibiting effect.

(*c*) When 20% heat-treated (under 500°C) natural zeolite powder is used, AAR in concrete can be inhibited efficiently.

(*d*) When the alkali content in cement is as high as 2·2%, if 30% natural zeolite powder with a specific surface area of 7000 $cm^2/g$ is used, AAR in concrete can be inhibited whatever kind of aggregate is used.

(*e*) Natural zeolite powder can produce a better inhibiting effect on AAR than slag – as good as fly ash, but not quite as good as silica fume. In particular, for an aggregate with very high alkali reactivity (e.g. aggregate B), natural zeolite powder can produce better inhibiting effect on AAR than fly ash or slag, because of higher chemical reactivity than the latter.

(*f*) For reactive aggregate from the Yong Dinghe River region in Beijing, when the dosage of natural zeolite powder (with a specific surface area of about 7000 $cm^2/g$) is more than 10%, the expansion of the mortar bar at 90 and 180 days is below ASTM limits. This means that harmful AAR in concrete can be prevented.

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**Discussion contributions on this paper should reach the editor by 25 September 1998**